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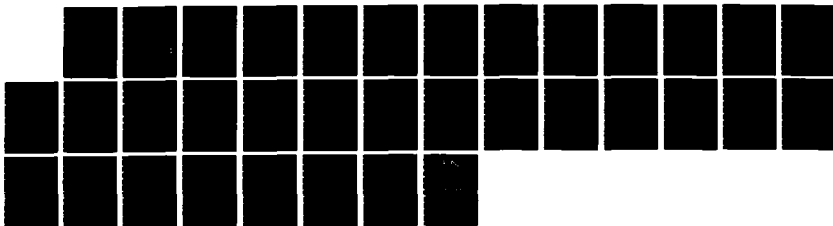
ACID-CATALYZED DEGRADATION OF
PPOLY(2-BUTYL-136-TRIOXOCANE(U) MASSACHUSETTS UNIV
AMHERST DEPT OF POLYMER SCIENCE AND ENGINEERING
J C CHIEN ET AL 21 OCT 85 TR-11

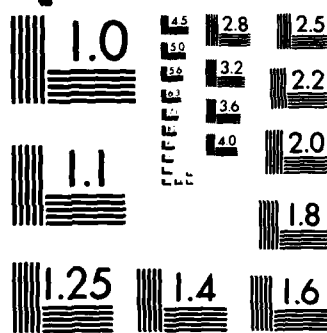
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TECHNICAL REPORT NO. 11

Acid-Catalyzed Degradation of Poly(2-butyl-1,3,6-trioxocane)

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Acid-Catalyzed Degradation of Poly(2-butyl-1,3,6-trioxocane)

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Synopsis

Acid catalyzed degradation of poly(2-butyl-1,3,6-trioxocane) (**1**) has been studied. With ethyl tosylate as the catalyst, the cyclic monomer **2** was the major product. The minor products are cis and trans isomers of $C_3H_7CH=CH-OCH_2CH_2OCH_2CH_2OH$, and three stereoisomers of $C_3H_7CH=CH-OCH_2CH_2OCH_2CH_2O-CH=CH-C_3H_7$ elucidated by 1H and ^{13}C NMR, IR, electron impact and chemical ionization MS, and in the case of **2** also by comparison with an authentic sample. With 98% H_2SO_4 as the catalyst **2** is only a minor product. The major products are diethylene glycol, valeraldehyde, and 1,4-dioxane with some 2-butyl-1,3-dioxolane. Capillary GC/Mass spectrometry led to identification of the following less abundant products: tri-n-propylbenzene, α,β -unsaturated aldehydes and cyclic dimer. The products of H_2SO_4 -catalyzed decomposition of polymer were also obtained by heating monomer **2** with H_2SO_4 . A detailed mechanism for the formation of the 8-member ring **2** in the decomposition is proposed which involves unzipping proceeds via open carbocation intermediates. According to the principle of microscopic reversibility, the same open carbocation is the propagating species in the polymerization of **2** under similar conditions.

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Introduction

Polyacetals, owing to the acid sensitivity of the acetal linkage, are attractive candidates for end uses in which acid sensitivity is a desirable property, e.g. photo- or electron-resists. Many polysaccharides belong to this general class and owe many of their special properties to the acetal linkage. An example is the α, β anomerism which distinguishes the acetal (glycosidic) linkages of starch and cellulose. Simple acetal polymers were first described in 1935 by Hill and Carothers who prepared them by acid-catalyzed condensation of aldehydes with diols.¹ But most of the modern synthesis has involved acid-catalyzed ring opening polymerization of cyclic acetals.² Acid-catalyzed depolymerization, the hallmark of this class of polymer has been relatively little studied,^{3,4,5} though many cases of polymerization in which monomer and polymer equilibrate are reported.² We report here a study of acid-catalyzed decomposition of poly(2-butyl-1,3,6-trioxocane) (1) under two sets of conditions: mild leading to depolymerization, and drastic leading to more profound degradation. A mechanism for depolymerization involving open chain oxy-carbocation intermediates operates.

Experimental Section

General

Infrared spectra were recorded with a Perkin-Elmer 1420 spectrometer and calibrated using the 1601 cm^{-1} band of polystyrene. UV spectroscopy was

performed using a Perkin-Elmer Lambda Array 3840 spectrophotometer. NMR samples were dissolved in CDCl_3 with internal tetramethylsilane standard, and spectra were obtained using Perkin-Elmer R-12 and Varian Associates XL-300 instruments. Off-line gas chromatography was carried out on a Hewlett-Packard 5790A chromatograph using a Foxboro Super Pak II 6 ft x 1/8 in o.d. column, temperature programmed (30° for 3 min, 30° to 200° at 20°/min, 200° for 10 min, carrier helium flow 25 mL/min). Ethyl tosylate from Aldrich Chemical Co. was dried over P_2O_5 prior to use. Concentrated sulfuric acid (98%) Fisher Reagent grade, was used as supplied.

Poly(2-butyl-1,3,6-trioxocane) (1)

Polymer was prepared by condensation of valeraldehyde and diethylene glycol as described previously.⁶ Molecular weight (\bar{M}_n) was estimated by determination of active hydrogen in well-dried samples which were treated with excess lithium aluminum hydride in THF to give hydrogen gas which was measured volumetrically. Two hydroxyl end groups per polymer chain were assumed. Molecular weights were always near 1800.

Thermogravimetric Analysis

Five mg polymer samples were decomposed using a Perkin-Elmer TGS-II instrument under a nitrogen flow of 0.05 mL/min. Solutions of ethyl tosylate in polymer were prepared by mechanical mixing. The resulting solutions showed no decomposition at room temperature over periods of 5 - 10 min.

Ethyl-Tosylate-Catalyzed Degradation

A solution of 1.2 weight % ethyl tosylate in 9.4 g poly(2-butyl-1,3,6-trioxocane) was heated in a small vacuum distillation apparatus from room temperature to 200° over a period of 1 h and then held at that temperature

until no more volatile product distilled. Volatile degradation products were distilled at 0.24 mm as they were formed. Distillate temperature was determined using a still head thermometer; three fractions of broad boiling range were collected (see Table I).

Redistillation of the first fraction gave a chromatographically pure colorless liquid, b.p. 233° at 760 torr (54 - 56 at 0.65 torr), identified as 2-butyl-1,3,6-trioxocane (2): IR(film) 2950-2870 s, 1450 m, 1375 m, 1310 s, 1150 s, 1080 s, 990 cm^{-1} s; ^1H NMR(CDCl_3) δ 4.58 (1H, t, acetal H), 3.71 (8H, m, $-\text{OCH}_2\text{CH}_2\text{O}-$), 1.60 (2H, q, $\alpha\text{-CH}_2$), 1.32 (4H, m, β and γ CH_2 's), 0.91 ppm (3H, t, CH_3); ^{13}C NMR(CDCl_3) δ 108.2 (d, C_1), 74.0 (t, C_5 and C_7), 70.9 (t, C_4 and C_8), 36.2 (t, C_α), 27.5 (t, C_γ), 23.0 (t, C_β), 14.6 (q, CH_3); mass spectrum Table I. Anal: Calc'd. for $\text{C}_9\text{H}_{18}\text{O}_3$: C, 62.03; H, 10.41. Found: C, 62.05; H, 10.44.

Sulfuric Acid-Catalyzed Degradation

Degradation was conducted in a fashion similar to that described above for ethyl tosylate catalysis except that polymer (1 g) was dropped into the still pot which contained 10 mg conc. sulfuric acid at 150° or 200°, over a period of 25 min. Volatile products were collected as a single brown liquid fraction (200° - 71% recovery, 150° - 59% recovery) and a small amount of colorless liquid in a downstream liquid nitrogen trap. The still pot residue was a black tar. After initial GC and spectroscopic analysis, the volatile products were washed once with excess water to remove diethylene glycol, dried (Molecular Sieve 3A), and residue was reanalyzed.

2-Butyl-1,3-dioxolane (3)

Valeraldehyde (43.0 g, 0.5 mole), ethylene glycol (34.3 g, 0.55 mole) and

benzene (100 ml) were introduced into a 3-necked flask fitted with a Dean-Stark trap and gas inlet tube. With magnetic stirring, HCl (0.018 g, 50 mmole) of HCl was added as catalyst. One hr reflux sufficed to remove 84 mL water. HCl was removed at 20 - 30 torr at room temperature. Distillation at atmospheric pressure yielded 41.7 g of **3** (64%) between 149° and 152°. Trace amounts of water in the product were removed by treatment with LiAlH_4 .

Identification of **3** is by elemental analysis, calc'd. for $\text{C}_7\text{H}_{14}\text{O}_2$: C, 64.58; H, 10.84; Found: C, 64.57; H, 10.62; ^1H NMR(CDCl_3) δ 4.84 (1H, t, H_2), 3.82 (4H, m, $-\text{OCH}_2\text{CH}_2-$), 1.64 (2H, m, $\alpha\text{-CH}_2$), 1.39 (4H, m, β and γ CH_2 's), 0.91 ppm (3H, t, CH_3); ^{13}C NMR(CDCl_3) δ 105.6 (C_1), 65.7 (C_3 and C_4), 34.5 (C_α), 27.1 (C_β), 23.5 (C_γ), 14.8 ppm (C_δ), and IR: 2960, 2880, 2760, 1470, 1415, 1220, 1150, 1130, 1070, 1040 and 970 cm^{-1} .

GC/MS Measurements

Degradation products were analyzed using a Hewlett-Packard 5985A instrument equipped with 12 m x 0.25 mm SE-30 fused silica capillary column. Samples were diluted by a factor of 10^3 in methylene chloride with anthracene- d_{10} as a mass standard. Carrier gas flow was 1 mL/min and the oven temperature was programmed from 32 to 200°C at 20°C/min. Both electron impact (70 ev) and chemical ionization (CH_4 reagent gas) were employed.

RESULTS

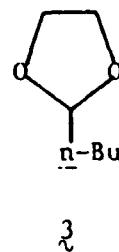
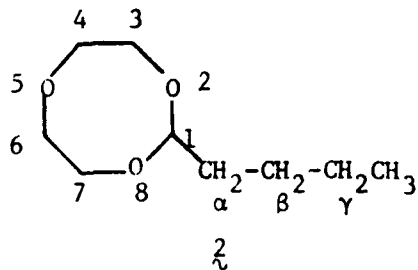
Thermogravimetry revealed the expected acid sensitivity of **1** clearly. Samples prepared with *p*-toluene sulfonic acid decomposed too quickly to be analyzed. Ethyl tosylate, neutral itself but able to generate acid at elevated temperature, proved to be a suitable acid for these studies. In the

absence of acid, when heated at 20°/min from ambient, 1 exhibited initial weight loss at ca 200°C and decomposition was not complete until a temperature of 370° was reached. A sample which contained 5% ethyl tosylate exhibited initial weight loss at ca 100° and 100% weight loss at only 210°C.

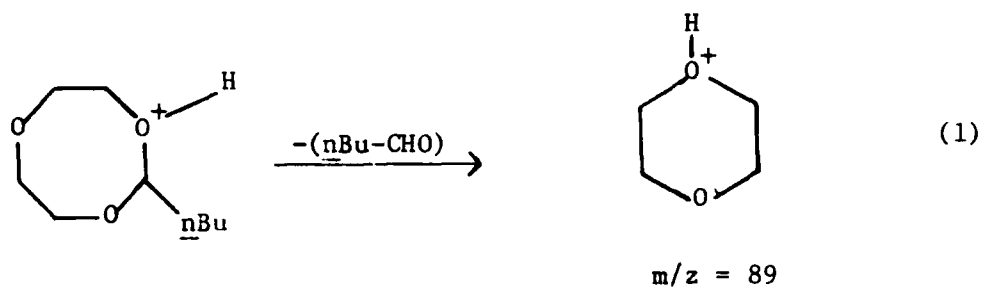
Ethyl Tosylate-Catalyzed Degradation

To determine products of acid-catalyzed decomposition we heated a solution of 1.2% ethyl tosylate in the polymer to 200°C in a distillation apparatus and distilled the volatile products at 0.25 torr as they formed. The fraction's collected are described in Table I. Initial GC investigation showed three fractions along with a few very minor components. Comparison with authentic samples demonstrated the absence of valeraldehyde, 2-butyl-1,3-dioxolane (3), and 1,4-dioxane. GC/MS analysis using a 12 meter SE-30 capillary column resolved the less volatile fractions into two and three components each (Fig. 1). The molecular and fragment ions observed for these components are presented in Table II.

The major component failed to give a molecular ion under electron impact conditions, but CI revealed a molecular weight of 174. This and the fragment ions are consistent with the 2-butyl-1,3,6-trioxocane structure 2. In



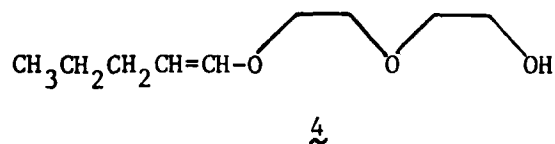
particular the base peak at $m/z = 89$ arises from a particularly characteristic fragmentation of crown ether acetals described by Hancock et al.⁷ eq. 1.



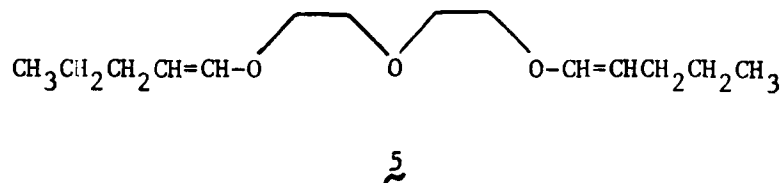
^1H and ^{13}C NMR data and chemical ionization MS (Figure 2) confirm structure 2 with which the IR spectrum and elemental composition are in full accord (see experimental section).

Structures 4a, b and 5a - c were deduced using mass spectral and ^1H NMR data. Compounds 4a and 4b are isomers of 2 and have the nearly identical mass spectra expected of geometrical isomers. Their increased concentration in degradation fractions B and C (Table I) corresponds to an increase in the intensity of O-H stretching in the infrared. Along with O-H stretch, an absorption in the C=C stretch region at 1670 cm^{-1} , with the enhanced intensity consistent with a vinyl ether appeared. ^1H NMR spectra of fractions B and C exhibited the downfield doublets expected for the cis and trans isomers of a vinyl ether α -proton, $-\text{O}-\text{CH}=\text{CH}-$, at δ 6.06 and 6.37 ppm.

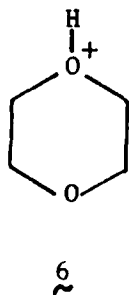
Table III lists all ^1H NMR absorptions and their assignments. The ^1H NMR data along with molecular weights from MS allowed assignment of the isomeric GC fractions 4a and 4b as the cis and trans isomers corresponding to 4 while



the three isomeric GC fractions 5a - c were assigned as the three stereoisomers of 5.

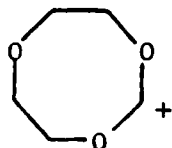


Mass spectral data listed in Table II confirm these assignments. Ions at mass 89 and 73, 6 and 7, respectively, are abundant and act as a signature

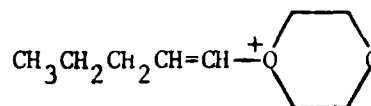


for the diethylene glycol moiety.⁸ Monoether 4 produced small amounts of the 117 ion (7) (rel abund 5 - 6%) but this is a major product of diether

fragmentation. CI produces ion 2 ($m/z = 157$) from the diethers. Scission α ,



8



9

β to ether oxygens produces C_4H_9^+ (57) and C_4H_7^+ (55).

Partially degraded polymer was examined using gel permeation chromatography. When degradation was interrupted at 38% completion (estimated by weight of residue in still pot), comparison by GPC showed that the molecular weight of the remaining polymer was substantially lower than the starting polymer ($M_n = 1800$).

Sulfuric Acid-Catalyzed Degradation

When polymer 1 was degraded by dropping onto hot 98% sulfuric acid at 200°C and 0.25 torr, a far more complex product mixture was obtained. One gram of polymer afforded 0.71 g of a light yellow-brown distillate accompanied by 0.1 - 0.2 g of colorless liquid collected from the downstream liquid nitrogen trap. Degradation at 150° yielded only 59% volatile products. Gas chromatographic analysis of the trap contents using authentic samples for selective enrichment of the product mixture revealed valeraldehyde and 1,4-dioxane as the major components followed by diethyleneglycol (10). Little or no 2-butyl-1,3-dioxolane was detected.

Gas chromatographic analysis of the contents of the distillation receiver revealed a complex mixture of which diethyleneglycol appeared to be the major

component. IR and ^1H NMR spectra of the distillate exhibited strong absorption attributable to 10 and its identity was later confirmed using GC/ms (see below). Diethyleneglycol comprised ca 50% of the total degradation products.

To increase the relative concentration of the many higher molecular weight products, the distillate was washed in a separatory funnel with water and subsequently dried over 3A Molecular Sieve. GC Analysis revealed that 10 along with lower molecular weight water-soluble components were removed selectively. When the washed product mixture was analyzed by GC/MS, thirteen components were resolved on the SE-30 capillary column, Figure 3.

The water wash decreased the relative intensity of saturated aldehyde carbonyl absorption at 1730 cm^{-1} in the infrared but enhanced absorptions at 1695 and 1645 cm^{-1} which we assign as $\text{C}=\text{O}$ and $\text{C}=\text{C}$ stretch of α,β -unsaturated aldehyde. The water-washed products exhibited ^1H NMR absorptions at δ 9.36 s, 6.47 t, 2.35 m, and 2.22 ppm m consistent with the partial structure below.



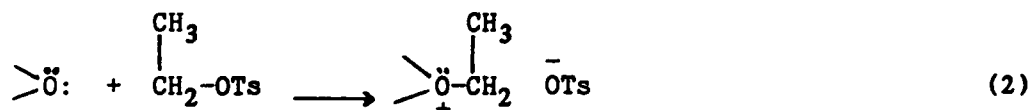
Analysis of the mass spectra, Table IV, then leads to the structural assignments in Table V. Structure numbers correspond to GC peak numbers. Diethylene glycol was identified by enrichment of the product mixture with authentic material as well as by its mass spectrum which matched that described in the literature. As mentioned above, the abundant ions at 89 and 72 serve as a signature for 10. The tri-n-propylbenzene structure fits the

mass spectrum of peak 15 well, the expected main fragmentation occurring at a benzylic bond to give the base peak at $m/z = 175$. The $C_7H_7^+$ ion at $m/z = 91$, diagnostic for aromatics was also observed. The mass spectrum of peak 14 agrees well with that expected for the α,β -unsaturated aldehyde 14 (an aldol condensation paroduct of valeraldehyde) suggested by IR and 1H NMR. Some of the observed fragment ions are accounted for by the fragmentation points shown in Table V. In addition $M-CO$ ($m/z = 126$) and McLafferty rearrangement ions, $Bu-CH=C=C(H)OH$ ($m/z = 112$), were observed. GC peaks 16a - d were assigned to the multiple condensation stereoisomers corresponding to formula 16 (Table V) on a similar basis. Finally peak 13 gives the unmistakable signature for the diethyleneglycol moiety in its fragmentation pattern ($m/z = 89, 73$). In addition ions 8 ($m/z = 117$) and 2 ($m/z = 157$) are present as well as protonated cyclic monomer at $m/z = 175$. No molecular ion was observed but the M -valeraldehyde peak, expected on the basis of the report of Hancock et al.,⁶ was observed at low relative abundance. Cyclic dimer is an expected equilibration product and seems a reasonable assignment on the basis of these considerations and its expected volatility.

Finally, to establish the relationship between ethyl tosylate and sulfuric acid catalysis, the principal product from ethyl tosylate-catalyzed degradation, 2, was subjected to the conditions under which sulfuric acid-catalyzed degradation had been carried out. Gas chromatographic, IR, and 1H NMR analysis of the product mixture showed that it was virtually identical to that produced by sulfuric acid-catalyzed degradation of the original polymer, 1. Scheme 1 summarizes our findings on degradation products under acid catalysis.

DISCUSSION

Identification of all the major and many minor products of acid-catalyzed degradation under two sets of conditions provides a detailed picture of the degradation process. Ethyl tosylate clearly behaves as the milder catalyst and operates under nearly anhydrous conditions. TGA experiments show that pure ethyl tosylate does not decompose to the much less volatile toluene-sulfonic acid when heated. When a 5 mg samples was heated in a TGA instrument at 200° under a nitrogen flow of 0.06 mL/min, ethyl tosylate, bp 173° (15 torr) evaporated completely within 5.5 min. Thus, substantial amounts of ethyl tosylate may be lost by vaporization. Catalysis presumably arises mainly owing to alkylation of other oxygens (eq. 2) which is effectively equivalent to protonation.



Since our ethyl tosylate, polymer, and glassware were rigorously dried, ethyl tosylate-catalyzed decomposition proceeded under as nearly anhydrous conditions as possible. In contrast, 100% of the sulfuric acid used is effective as catalyst, and the small amount of water in our 98% H₂SO₄ may play an important role in degradation. In addition, stoichiometry requires water to be produced along with the observed degradation products under these conditions.

Major Pathways

Structural changes in ethyl tosylate-catalyzed degradation are minimal,

the major pathway leading to cyclic monomer. Clean depolymerization of poly(1,3,6-trioxocane) itself as well as that of poly(1,3-dioxocane) to give cyclic monomers under relatively mild conditions, BF_3 catalysis, have been described by Bushfield and Lee.³ Under more drastic conditions, more acid and traces of water, with sulfuric acid-catalysis more profound changes occur. Formation of cyclic monomer (2) is probably the fastest initial pathway. However, our demonstration that 2 gives the same product mixture as the original polymer 1 when treated with sulfuric acid at 200° does not require that 2 be the direct precursor of further degradation products. Under acidic conditions polymer, oligomers-cyclic and linear, and cyclic monomer are known to equilibrate. Thus, although 2 is a plausible precursor of the products of sulfuric acid-catalyzed decomposition, oligomers and even polymer could contribute as well. These products of further degradation arise from complete cleavage of all acetal linkages to give diethyleneglycol, the major product, and valeraldehyde. Acid catalyzed-aldol condensation to give products such as 14, 15, and 16a - d is the fate of most aldehyde under our conditions. Small amounts of diethyleneglycol are converted to 1,4-dioxane and cleaved to ethylene glycol which condenses with valeraldehyde to give cyclic acetal 3. Under these conditions only small amounts of cyclic monomer (2) and cyclic dimer (13) distill before further reaction. These pathways are summarized in Scheme 2.

Degradation Mechanism

Several different sets of products from acid catalyzed unzipping of 1 as is observed in the presence of ethyl tosylate.

- a) an equimolar mixture of 3 + ethylene oxide

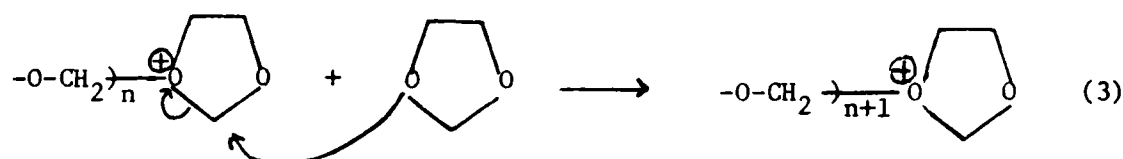
b) an equimolar mixture of 1,4-dioxane + valeraldehyde

c) a 2:1 mixture of 2 + 1,4-dioxane

d) 2-butyl-1,3,6-trioxocane

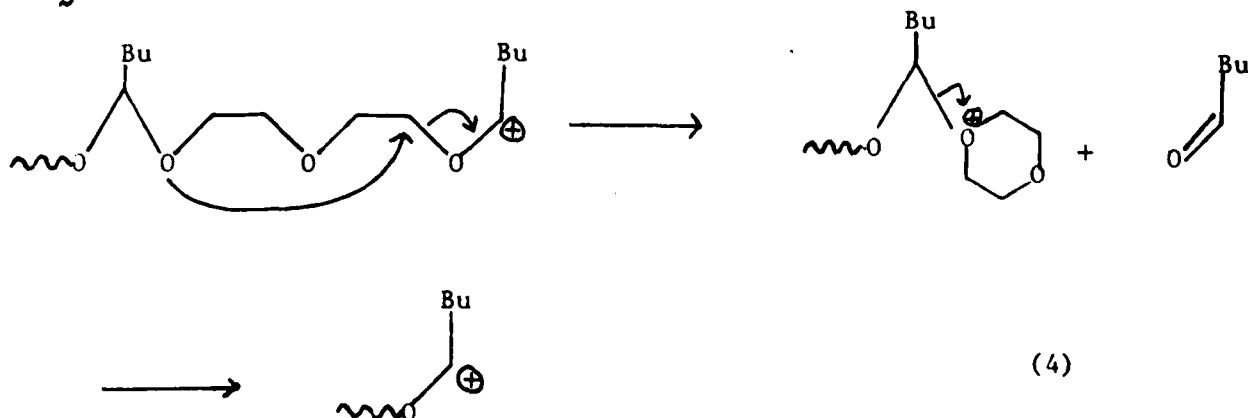
From a thermodynamic point of view, set a and trioxocane 2 are disfavored owing to ring strain destabilization^{of} three- and eight-membered rings, while sets b and c are most favored. Thus, trioxocane, 2, with its strained 8-membered ring, must be a product of kinetic control.

Penczek on the basis of thorough investigation of acid-catalyzed polymerization of 1,3-dioxolane has concluded that it proceeds via nucleophilic displacements at cyclic oxonium ion termini, eq. 3

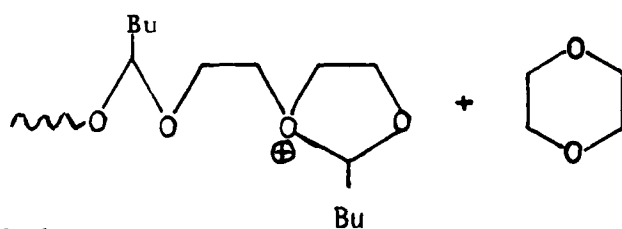
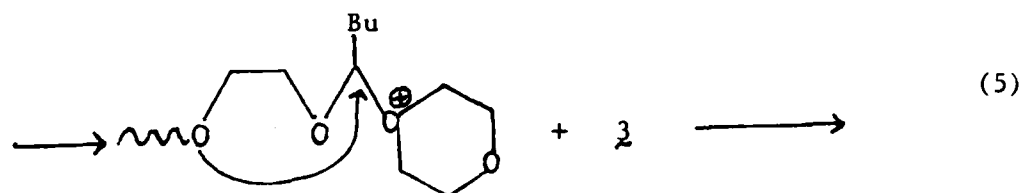
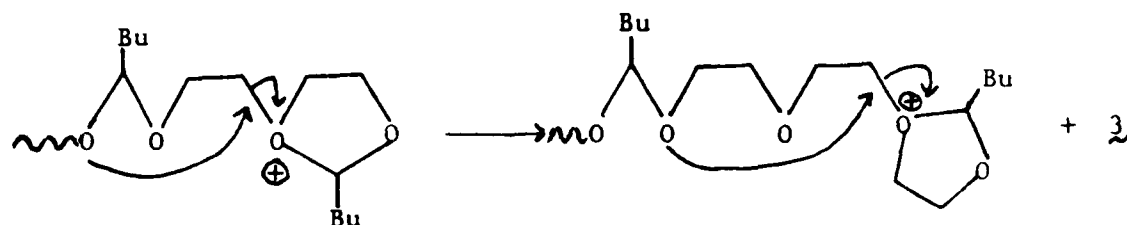


If we assume analogous degradation pathways for ethyl tosylate-catalyzed degradation of 1 we must consider the pathways shown in equations 4 -6.

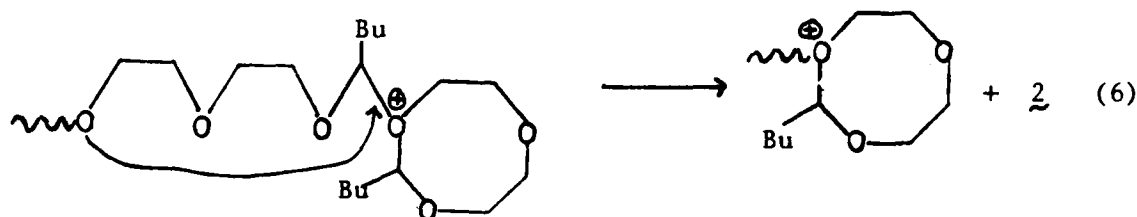
Path b



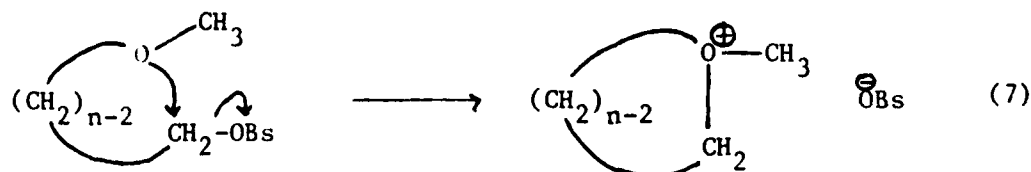
Path c



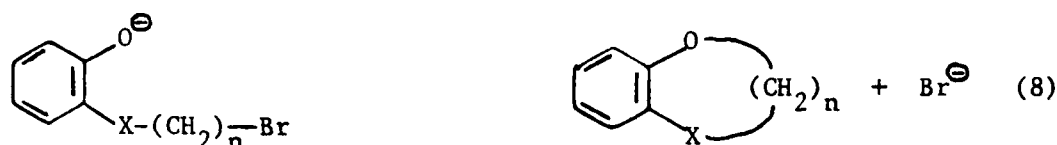
Path d



Path d requiring neighboring group participation with 8-membered ring formation should be strongly disfavored kinetically. Winsteins¹⁰ classic study of methoxyl participation, eq. 7 showed the rate at a maximum for 5-membered ring formation and dropping steeply on going to 6- and then 7-



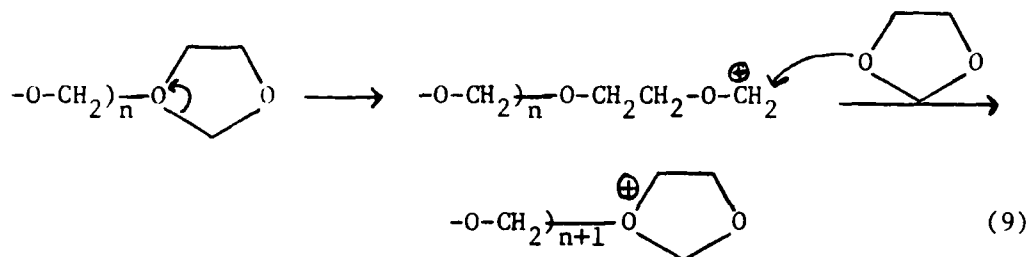
membered rings. The 8-membered ring case, $n = 8$, was not studied. The detailed investigation of ring formation by Illuminati and his coworkers^{11,12} show that formation of 8-membered rings is highly disfavored kinetically compared to formation of 5- and 6-membered rings. In closure of (ω -bromoalkyl)malonate anions to carbocycles the 5/8 rate ratio is ca. 10^7 the 6/8 ratio 10^4 . Medium rings such as cyclooctane are destabilized by transannular H-H interactions. Replacement of methylenes with oxygen atoms lowers the strain. Thus a trioxocane should be less destabilized relative to linear polymer than is cyclooctane. Illuminati et al.¹¹ have evaluated the oxygen effect in eq. 8 by studying the effect of replacing $X = CH_2$ with $X = O$.



For 8-membered ring formation, replacing $-CH_2-$ with $-O-$ led to a ca 6-fold rate increase, a small factor compared to the 5/8 and 6/8 rate ratios of $10^{5.5}$ and $10^{3.5}$ when $X = CH_2$. In light of the large kinetic disadvantage of 8-membered ring formation exclusive formation of trioxocane attracts notice. We note that this is the only pathway which proceeds exclusively via acetal C-O bond cleavage.¹³ It seems doubtful to us that this factor would be large enough in S_N2 type reactions to overcome the large rate factors posed to 8-membered ring formation.

Consideration of the structural differences between 1,3-dioxolane and 2-butyl-1,3,6-trioxocane monomers strongly suggests a different pathway for the

latter monomer. Penczek's work suggests strongly that the energy (and rate) differences between the cyclic displacement (eq. 3) and open α -oxycarbocation (eq. 9) mechanisms for 1,7-dioxolane polymerization are not large.



In our case the presence of an alkyl group at C₂ should simultaneously retard nucleophilic attack (eq. 3) owing to steric effects but accelerate formation of the α-oxycarbocation (eq. 9). This should easily be sufficient to tip the scales in favor of the latter mechanism. Thus, we conclude that the α-oxycarbocation pathway (Scheme 3) is the pathway for ethyl tosylate-catalyzed unzipping of polymer 1. Cyclization of the α-oxycarbocation 17 to a 5-membered ring should occur reversibly and proceed no farther owing to the unfavorable nature of cleavage to produce a primary carbocation.

Initiation by alkylation or protonation of acetal oxygen and cleavage to give chain end 17 will not occur preferentially at the chain end but will take place with roughly equal probability at every acetal oxygen in the polymer chain. Thus, molecular weight is expected to decrease as degradation proceeds in accord with our observation. Vinyl ether groups like those of 4 and 5 can be formed by loss of a β -proton from 17.

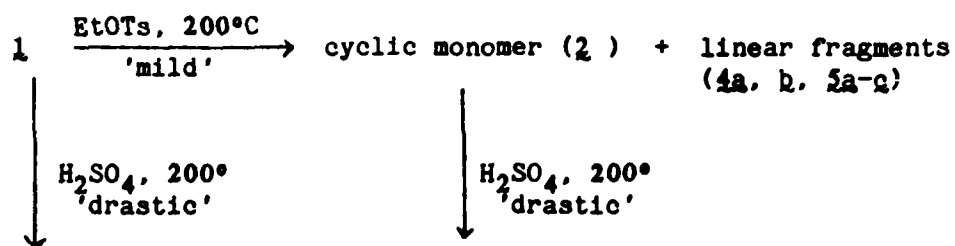
Polymerization Mechanisms

Polymerization of many cyclic acetals has been described but detailed knowledge of mechanism is confined to the case of 1,3-dioxolane (propagation step eq. 3).

The principle of microscopic reversibility forces us to conclude that, in contrast, polymerization of 2-butyl-1,3,6-trioxocane (2) in the presence of *p*-toluenesulfonic acid should proceed via open α -oxycarbocation intermediates.

Acknowledgement

The work was supported by ONR contract No. N00014-81-K-0611. A grant from the National Science Foundation covered part of the cost of the XL-300 NMR spectrometer.

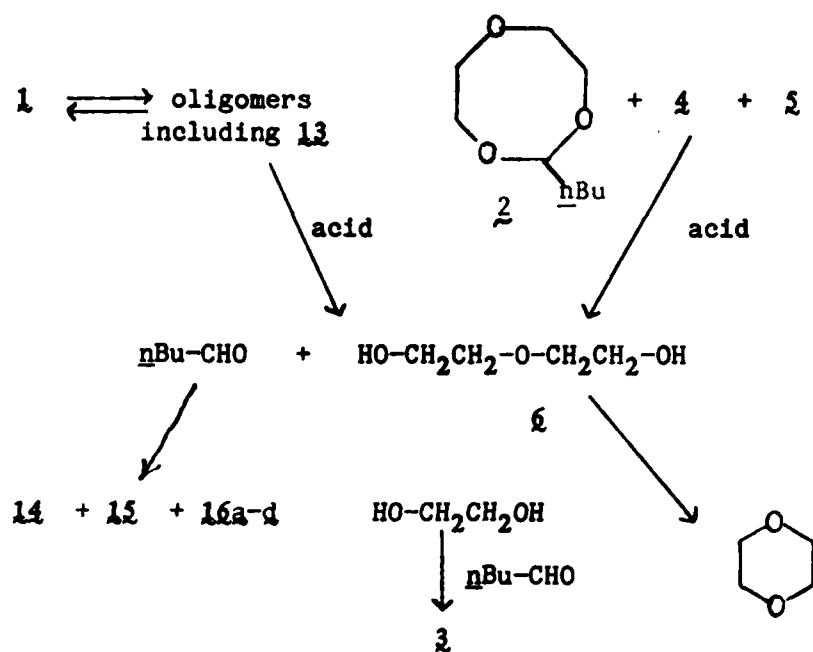


Valeraldehyde + Diethyleneglycol + Ethylene glycol (as cyclic acetal 3)

+ Aldol condensation products of valeraldehyde + Cyclic dimer

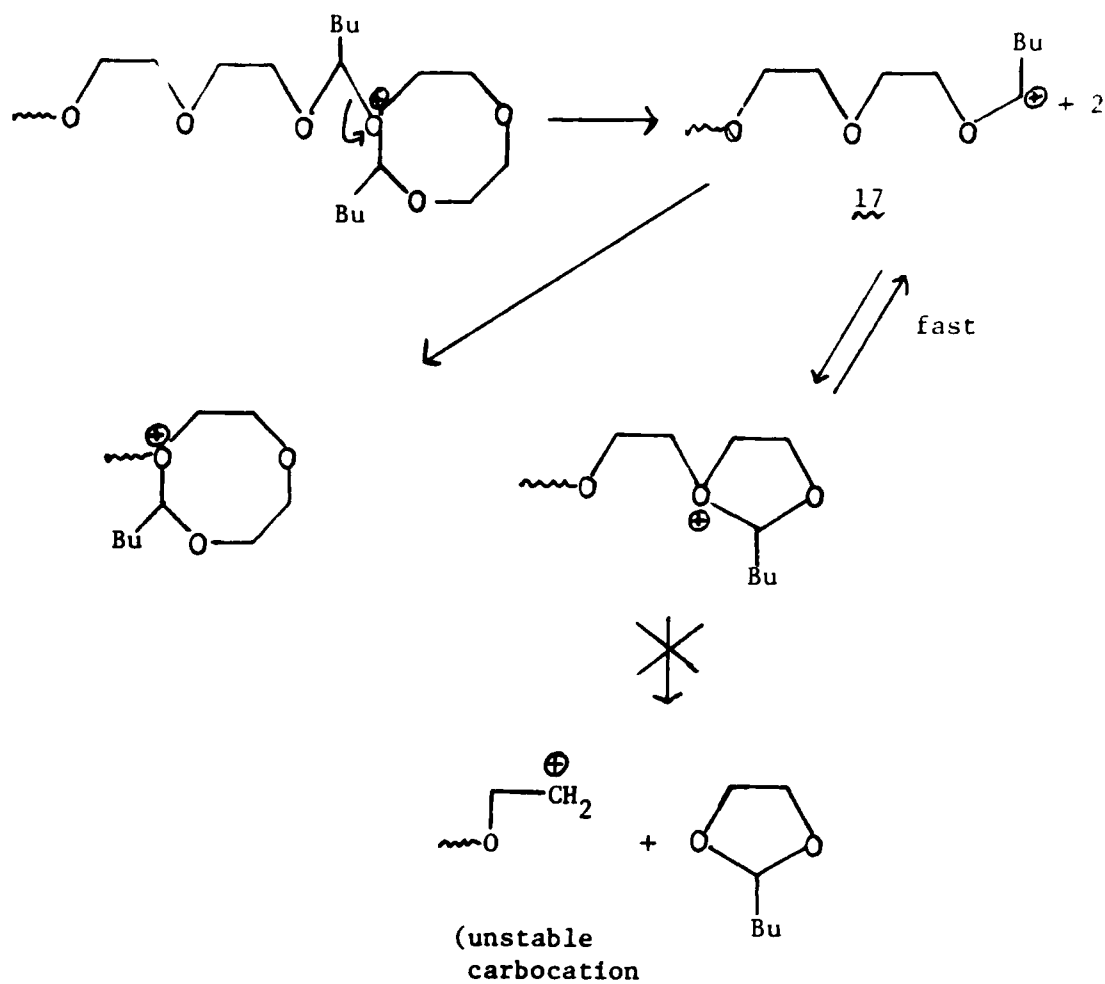
Scheme 1

Summary of product types as a function of conditions in degradation of poly(2-butyl-1,3,6-trioxocane) (1).



Scheme 2

Major pathways for acid-catalyzed degradation of
poly(2-butyl-1,3,6-trioxocane) (1)



Scheme 3

The α -oxycarbocation mechanism for unzipping of
poly(2-butyl-1,3,6-trioxocane)

Table I

Ethyl Tosylate-Catalyzed Degradation of Poly(2-butyl-1,3,6-trioxocane)

Fraction ^a	Boiling Range (°C)	Total Weight (g) ^b	Composition ^c		
			<u>2</u>	<u>4a, 4b</u>	<u>5a, 5b, 5c</u>
<u>A</u>	52-92	4.2	94	small	small
<u>B</u>	86-102	2.4	60	24	10
<u>C</u>	90-110	2.1	43	39	17

^aSample of 9.4 g polyacetal with 1.2 weight % ethyl tosylate heated at rt to 200° 1 h 12 min at 0.25 torr and volatile products distilled from the reaction flask.

^bResidue in reaction flask 0.4 g. No product collected in a downstream liquid nitrogen trap.

^cBased on percent of total peak area. Values are \pm 3%.

Table II

Mass Spectral Data for Products of Ethyl Tosylate-Catalyzed
Degradation of Poly(2-butyl-1,3-dioxolane)

GC Peak Number ^a	Molecular and Fragment Ions ^b	
	Electron Impact M/Z (rel. abund.)	Chemical Ionization M/Z (rel. abund.)
2 ~	73(31) 87(100) 117(21) 144(16)	45(22) 89(100) 117(28) 175(40)
4a ~	45(100) 57(23) 89(50) 174(6)	45(30) 55(54) 57(100) 89(48) 175(7)
4b ~	45(100) 57(21) 89(48) 174(5)	45(64) 55(53) 57(99) 89(100) 175(6)
5a ~	41(71) 45(38) 73(100) 117(50) 242(7)	55(55) 87(100) 73(46) 117(50) 157(34)
5b ~	41(63) 45(41) 73(100) 117(71) 242(21)	55(58) 57(100) 73(71) 117(54) 243(2)
5c ~	41(78) 45(43) 73(100) 117(40) 242(4)	55(54) 57(100) 73(34) 117(34) 157(41) 243(2) 157(40)

^aSee Figure 1, the number corresponds to the designation for the identified compound.

^bIons selected for listing on the basis of relative abundance and structural significance.

Table III

Proton NMR Signals and Assignments for Products of Ethyl Tosylate-Catalyzed
Decomposition of Poly(2-butyl-1,3,6-trioxocane) (1)

Chemical Shift δ , ppm	Peak Pattern	Coupling Const. J, Hz	Assignment
0.90	t	7	$-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
1.31	m		$-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
1.62	m		$-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
1.94	q	8	trans- $\text{CH}=\text{CHCH}_2\text{CH}_2\text{CH}_3$
2.00	q	8	cis- $\text{CH}=\text{CHCH}_2\text{CH}_2\text{CH}_3$
3.71	m		} $-\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{O}-$
3.88	m		
4.36	m		$\begin{array}{c} \text{H} \quad \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{O} \quad \quad \end{array} \quad (\text{cis})$
4.58	t		$\begin{array}{c} \text{O} \quad \quad \text{O} \\ \diagdown \quad \diagup \\ \text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \end{array}$
4.79	m		$\begin{array}{c} \text{O} \quad \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \quad \end{array} \quad (\text{trans})$
6.06	d	6.3	$\begin{array}{c} \text{H} \quad \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{O} \quad \quad \end{array} \quad (\text{cis})$
6.37	d	12.2	$\begin{array}{c} \text{H} \quad \quad \quad \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{O} \quad \quad \text{H} \end{array} \quad (\text{trans})$

Table IV

Mass Spectral Data for Products of Sulfuric Acid-Catalyzed Degradation
of Poly(2-butyl-1,3,6-trioxocane) (1)

GC Peak Number ^a	Molecular and Fragment Ions ^b	
	Electron Impact M/Z (rel. abund.)	Chemical Ionization M/Z (rel. abund.)
<u>3</u>	45(29) 57(6) 73(100)	69(42) 73(74) 87(31) 131(100)
<u>9</u>	45(90) 75(100) 76(53)	63(27) 73(36) 89(100) 107(45)
<u>14</u>	83(86) 97(48) 111(53) 125(100) 154(91)	99(17) 137(7) 155(100)
<u>2</u>	73(27) 87(100) 117(26) 144(24)	89(100) 117(25) 175(52)
<u>15</u>	91(21) 133(18) 175(100) 204(32)	
<u>16a</u>	69(48) 87(100) 93(10) 222(4)	
<u>16b</u>	137(100) 166(45) 193(14) 222(5)	
<u>16c</u>	137(50) 180(100) 193(25) 222(24)	69(4) 180(6) 207(10) 223(100)
<u>16d</u>	138(79) 165(16) 193(100) 222(37)	69(5) 179(3) 207(4) 223(100)
<u>13</u>	45(41) 89(100) 117(17) 175(35)	73(12) 89(78) 175(100)

^aSee Figure 2.

^bIons selected for listing on the basis of relative abundance and structural significance.

Table V

Products of Sulfuric Acid-Catalyzed Degradation of

Poly(2-butyl-1,3,6-trioxocane) 1.

Numbers correspond to GC peak numbers in Figure 2.

Chain fragments:

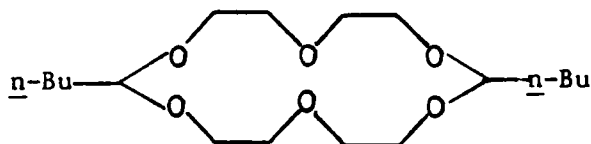
Valeraldehyde (11)

Diethylene glycol (10)

Cyclics:

Butyl-1,3-dioxolane (3)

Cyclic monomer (2)



Cyclic dimer (13)

Valeraldehyde condensation products:

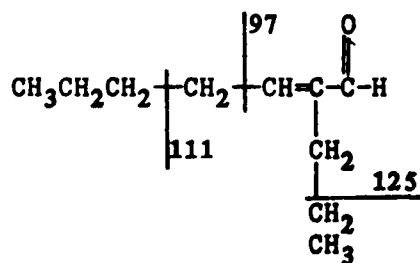
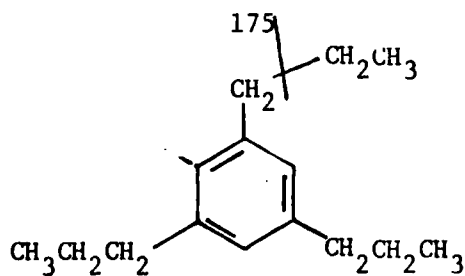
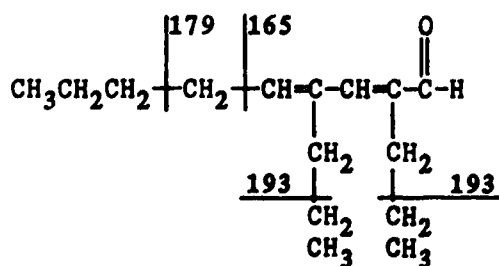
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Figure Captions

- Figure 1 Gas chromatogram of products from ethyl-tosylate-catalyzed degradation of poly(2-butyl-1,3,6-trioxocane) (1). Column 12 m x 0.25 mm SE-30 fused silica capillary, temperature 50 to 200°C at 20°/min, carrier gas He, 1 mL/min. Peaks are labelled to correspond to assigned structures in text. Peak X is anthracene-d¹⁰.
- Figure 2 Chemical ionization mass spectra of 2-butyl-1,3,6-trioxocane (3).
- Figure 3 Gas-chromatogram of water-washed products from sulfuric acid-catalyzed degradation of poly(2-butyl-1,3,6-trioxocane) (1). Column 12 m x 0.25 mm SE-30 fused silica capillary, temp. 50 to 200°C at 20°/min, carrier gas He, 1 mL/min. Peaks are labelled to correspond to assigned structures in the text. Peak X is anthracene-d¹⁰; other peaks are not identified.

Fig 1

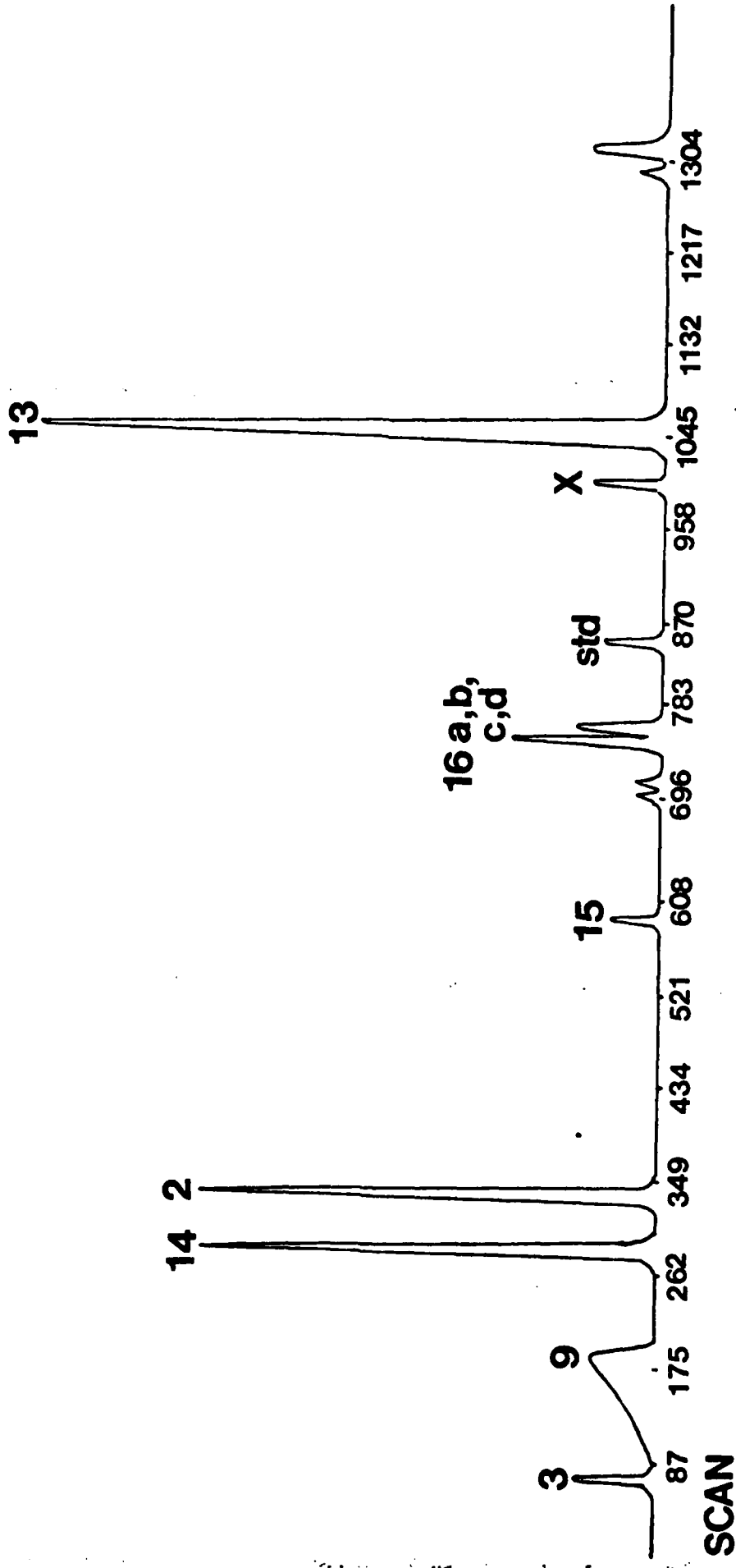


Fig. 2

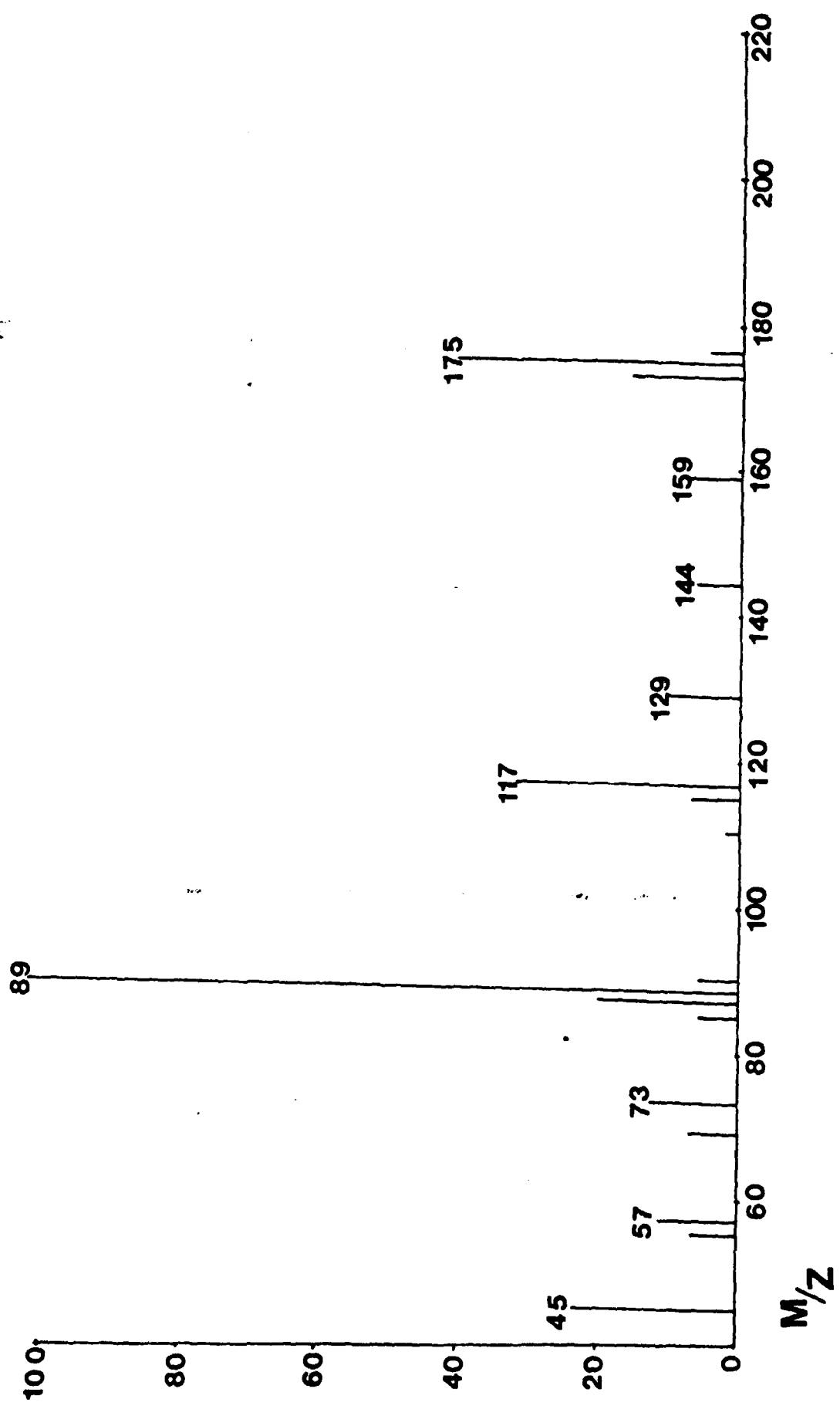
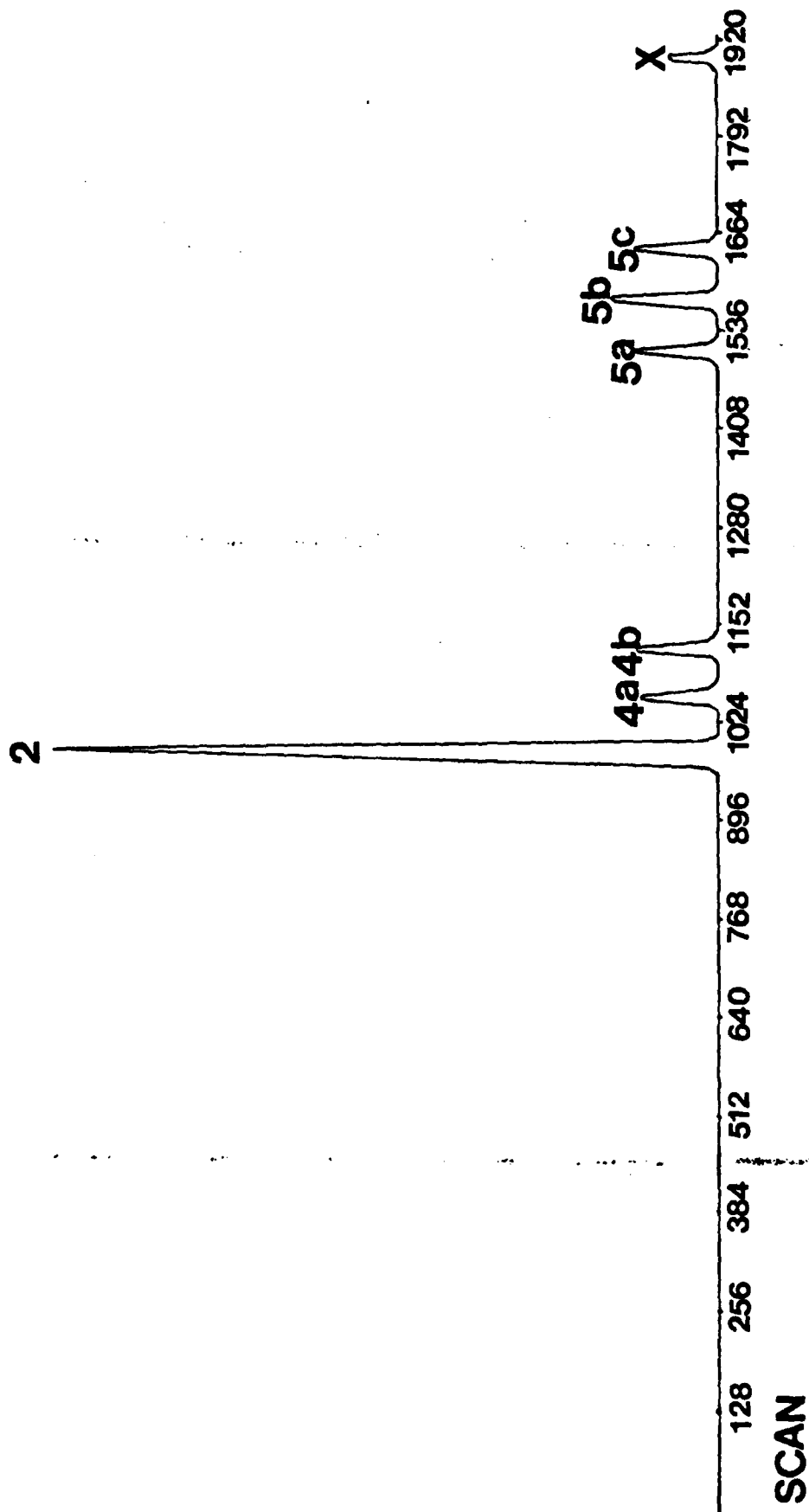


Fig 3



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13. In the presence of sufficient water the open α -oxycarbocation in pathway b could be intercepted obviating this problem.

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